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AKD Sizing Reversion: The Adsorption of the Volatile Products of Heated Alkyl Ketene Dimer onto Cellophane Part I: Impact on Sizing

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AKD SIZING REVERSION: THE ADSORPTION OF THE VOLATILE PRODUCTS OF HEATED ALKYL KETENE DIMER ONTO CELLOPHANE - Part I: IMPACT ON SIZING

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ABSTRACT

In an ideal AKD sizing system, the size cures with time and sizing increases. In practice, sizing may decrease with time and sizing may be variable. Thermal decomposition of AKD followed by deposition of degraded products in the paper may be the cause. Research reported here focused on the impact of volatile products from heated AKD on the sizing of a model paper substrate, cellulose film. Heating AKD produced material that migrated through the vapor phase. Adsorption of these volatile products produced sizing levels well below that of an AKD-treated control. AKD temperature was found to be statistically significant. Significant reduction in the water contact angle was not observed until the AKD temperature reached 150°C. When exposed to the volatile decomposition products, the initial water contact angle of film treated with AKD decreased from 104.4 +/- 2.7 degrees to 76.6 +/- 3.5 degrees. This was similar to the water contact angle (73.0 +/- 2.1 degrees) of a virgin cellulose film similarly exposed showing that the final contact angle was dependent on the composition of the volatile products. Therefore, thermal decomposition of AKD likely plays an important role in the determining the degree of sizing in the final product.

INTRODUCTION

The sizing of paper can be defined as "the process whereby a chemical additive provides paper products with resistance to wetting, penetration, and absorption by aqueous liquids"[1]. The primary types of sizing agents used currently in the industry are rosin-based and cellulose-reactive sizes. One example of a reactive size is alkyl ketene dimer (AKD) which has achieved wide use in the industry because of its broad applicability in a variety of products including those produced in alkaline papermaking systems. The research reported in this paper focused on the impact of the volatile products from heated AKD on the sizing of a model paper substrate, cellulose film.

In an ideal AKD sizing system, the size "cures" with time and sizing increases as the AKD continues to react with cellulose. However, in practice, the sizing may actually decrease with time and lead to considerable variability in sizing observed after paper manufacture. This loss in sizing has been labeled sizing reversion and has received extensive attention over the last several years.

The specific mechanism of AKD reversion is unclear. However, several processes have been suggested to explain the observed reversion. The most likely mechanisms from the literature are:

Hydrolysis of AKD to form the less efficient sizing ketone,[2]
Interaction of AKD with additives in the papermaking furnish,[3,4,5,6,7]
Migration of AKD or sizing within paper,[8,9,10]
Thermal decomposition of AKD during paper drying.[11]

There has been a significant amount of research conducted on sizing reversion caused by the first two mechanisms. However, relatively little effort has been focused on either the possible products of the decomposition or the vapor migration tendency of AKD itself. Since AKD is the dimer of two fatty acids, it seems plausible that the thermal breakdown of the dimer could reform the acid or generate other chemical compounds. Migration of AKD or decomposition products through the paper could influence the sizing in other parts of the sheet or throughout the diameter of a paper roll. Therefore, this research is focused on the thermal breakdown of AKD and the effect of the decomposition products on paper sizing.

It is known that a temperature gradient exists inside a roll of paper after manufacture. In the core of a roll, the temperature of the paper (and the AKD) will be close to the temperature of the last dryer drum. For some fine paper machines, this temperature may be as high as 110°C.[12] A redistribution of AKD within the roll could occur due to radial vapor migration of the AKD from the center of the roll along the temperature gradient and account for losses in sizing (Figure 1). This mechanism has been suggested for large molecules by Jensen and Neogi[8] who observed a sizing gradient from the inside of a paper roll sized with rosin. In addition, it was noted that the rosin content was lower at the center of the roll. A similar process can be envisioned if the AKD degrades and its decomposition products move through the paper roll. The current research was designed to answer questions as to AKD vaporization and/or decomposition driven by the temperatures that exist within a paper roll.

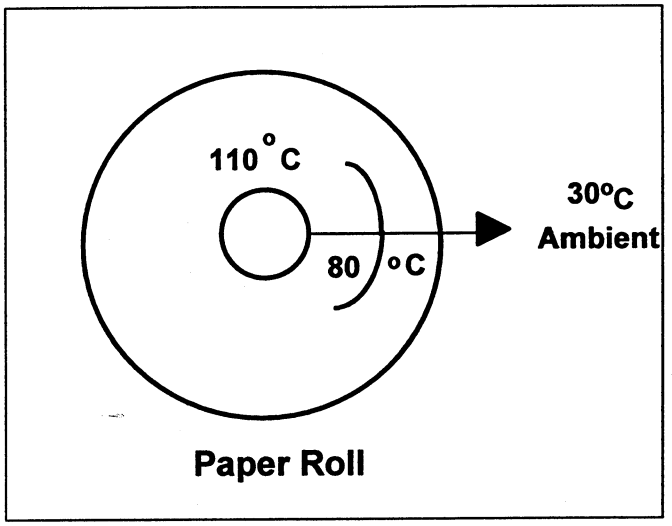

Figure 1. Hypothetical Temperature Profile of a Typical Paper Roll. After reelup, a temperature gradient is established with a hot center and cool edges. The temperatures and their position in the roll are arbitrary.

OBJECTIVE

The primary objective of this research was to determine the impact of the volatile products from heated AKD on the sizing of a model paper substrate, cellulose film. A second objective, identification of the volatile compounds, will be covered in a separate article.

EXPERIMENTAL APPROACH

The objective of the research was to determine if the heating of AKD created volatile material that could change sizing. Because paper is a very complex structure, a simpler substrate, cellophane, was used to emphasize the surface effects of the sizing agent. Water contact angle was selected for use as an indicator of changes in the degree of sizing. While other sizing tests have been used, water contact angle was selected as the most fundamental test available for this study. Solid AKD was used to simulate AKD located inside a dry roll of paper.

Solid AKD was heated in a controlled environment; cellophane was exposed to the volatile products from heated AKD to simulate the vapor migration and adsorption of these compounds in a paper roll. A schematic of the reaction cell is shown in Figure 2. Cellophane wrapped around a glass cold-finger condenser (Figure 3) acted as the adsorbate collector. After exposure, the cellophane was removed from the cold finger and conditioned in a constant temperature and humidity room (72°F, 50% R.H.) for 24 hours prior to contact angle analysis.

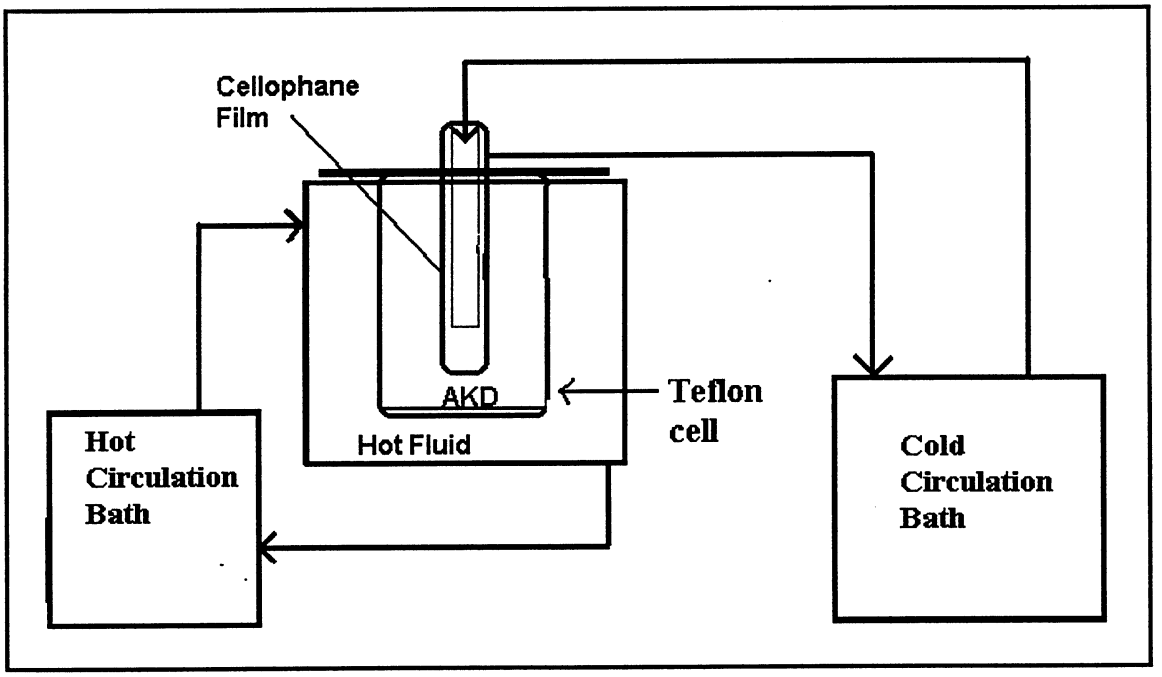

Figure 2. Volatile Product Collection Cell. Coolant enters at the top of the cold finger, flows through the inner tube to the bottom and exits at the top on the side. The outer shell contains the hot fluid (water, shown here, or sand for AKD temperatures above 100°C). AKD is placed in the Teflon cell at the beginning of an experiment. The cold finger containing the cellophane is then lowered into the Teflon cell and clamped for stability.

Contact angles were measured with an FTA-200 Dynamic Contact Angle Analyzer. Video images of the water drop were obtained at selected intervals over a five-minute period. Initial contact angles were defined as the contact angle of the water drop on the cellophane surface at the moment of contact of the drop with the surface.

The variables studied were the AKD temperature (T_h), the temperature of the cellophane assumed to be that of the cold finger (T_c), and the adsorption time (t_{ads}). A full factorial experimental design was employed. In all cases, the AKD temperature was higher than the film temperature to establish a positive temperature gradient between the heated AKD and the adsorption surface.

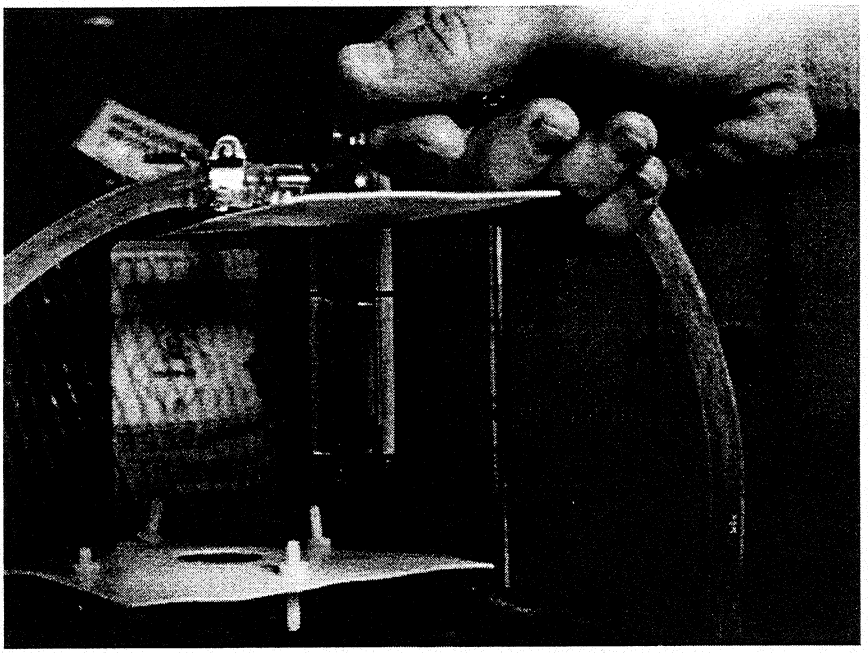

Figure 3. Cold Finger Adsorbate Collector. A small length of cellophane fits over the end of the cold finger and acts as the adsorption surface.

RESULTS AND DISCUSSION

Impact of Volatile Products on Untreated Cellophane

The results are found in Table I and Figures 4-7. Individual data points represent the mean of eight independent tests for water contact angle on each replicated sample. The 95% confidence interval is also shown for each replicate. A control sample of cellophane alone, i.e., without AKD in the cell and the experiment run under identical conditions (T_h = 150°C, T_c = 30°C, t_{ads} = 10 minutes), produced an initial contact angle of 37.2 +/- 2.7 degrees. A second control consisting of AKD treated cellophane produced an initial contact angle of 104.6 +/- 2.8 degrees. An analysis of variance of the data in Table 1 indicated a significant effect (95% confidence level) of AKD temperature (T_h) on contact angle. However, there was no significant effect of changing the film temperature (T_c) or adsorption time (t_{ads}) on the contact angle of cellophane. In addition, there were no interactions that were significant.

The results are summarized in Figure 4. In all cases, the contact angle is less than that provided by the direct AKD treatment. This indicates that AKD decomposes on heating and its decomposition products are less effective sizing agents than virgin AKD.

Table I. Variation in the Initial Water Contact Angle on Cellophane Upon Exposure to AKD Volatiles (+/- values represent the 95% confidence interval). The water contact angle is highest when the AKD temperature (T_h) is 150°C.

T_h, °C	80				150			
T_c, °C	30		65		30		65	
t, min.	30	60	30	60	30	60	30	60
Repl. 1 (n=8)	40.1 +/- 2.6	60.9 +/- 13.5	38.5 +/- 4.4	58.3 +/- 4.7	77.6 +/- 3.3	77.1 +/- 2.7	78.3 +/- 3.5	78.4 +/- 4.8
Repl. 2 (n=8)	57.8 +/- 5.6	46.3 +/- 6.6	54.2 +/- 3.7	48.0 +/- 3.2	68.4 +/- 3.1	72.6 +/- 1.6	62.2 +/- 5.7	65.0 +/- 5.0

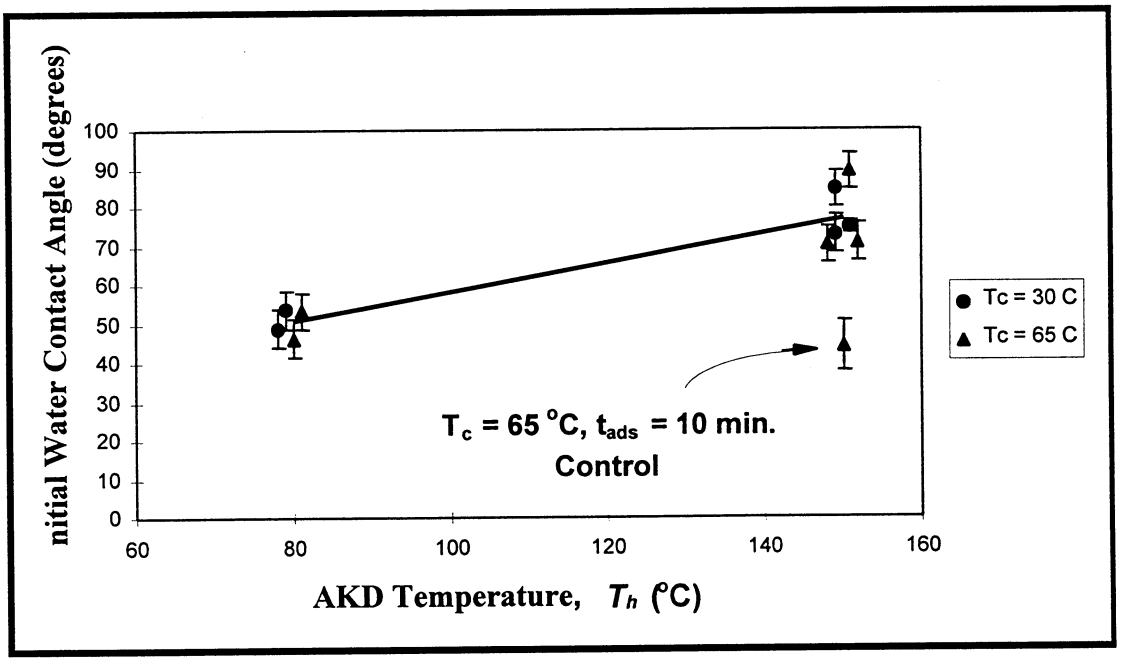

Figure 4. Effect of AKD Temperature (T_h) on the Initial Water Contact Angle of cellophane (see Table I for numerical values).

Changes in drop-aging time.

In Figure 5, the water contact angles of the adsorbates at each AKD temperature are plotted together versus the drop-aging time. The drop-aging time is the length of time the water drop sits on the cellophane during the contact angle experiment. A completely flat curve would exist for cellulose with AKD tightly bonded to the surface. Deviations with time are indicative of reduced levels of chemical bonding.

In general, all of the drop-aging curves have the same shape, and decrease at the same rate. The water contact angle is highest at short adsorption times and high AKD temperatures. This suggests that while the amount of material adsorbed increases with temperature, only a limited chemical reaction occurs between the volatile products and the cellulose surface.

Comparison with direct treatment with AKD.

It has been shown here that the surface energy of cellophane, i.e., the water contact angle, can be modified by adsorbing volatile products from heating AKD. The surface hydroxyl groups, which would normally interact with water and produce a low contact angle (high surface energy), can be modified by the adsorption of hydrophobic material that produces a higher contact angle (low surface energy). However, it remained open to question whether adsorption of volatile decomposition products gives a different effect than direct treatment of cellophane with AKD. The following results (Figure 6) compare the water contact angle of AKD-treated cellophane with the water contact angle obtained upon exposure to AKD volatiles (T_h = 150°C).

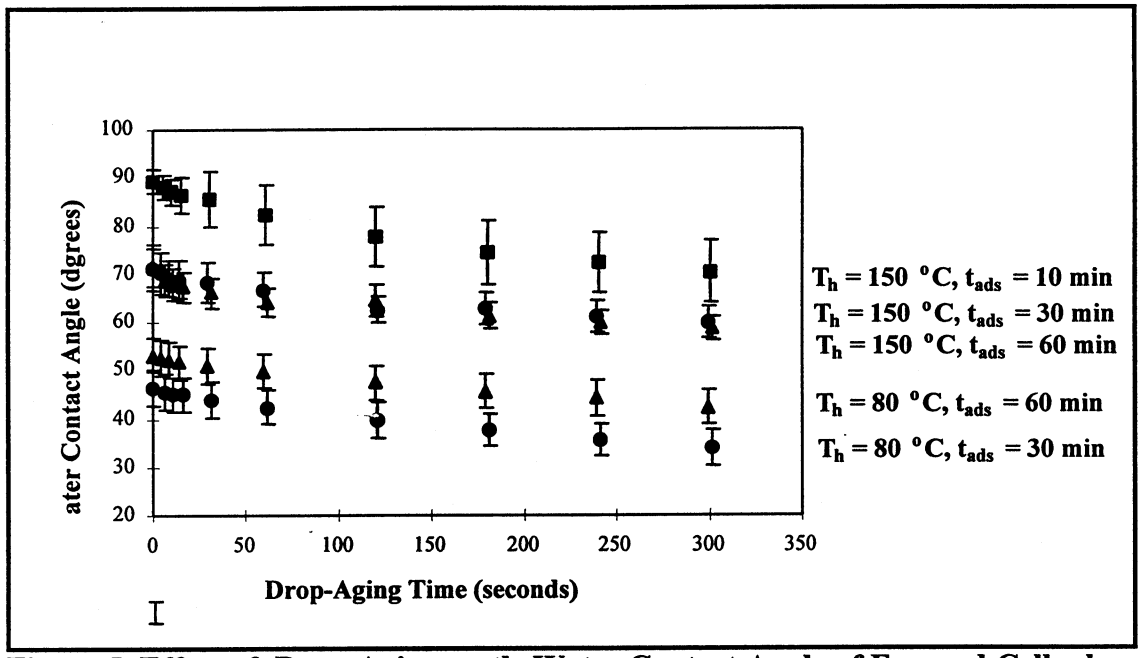

Figure 5. Effect of Drop-Aging on theWater Contact Angle of Exposed Cellophane: (T_c constant at 65°C, T_h = 80, 150°C; t_{ads} = 10, 30, 60 minutes).

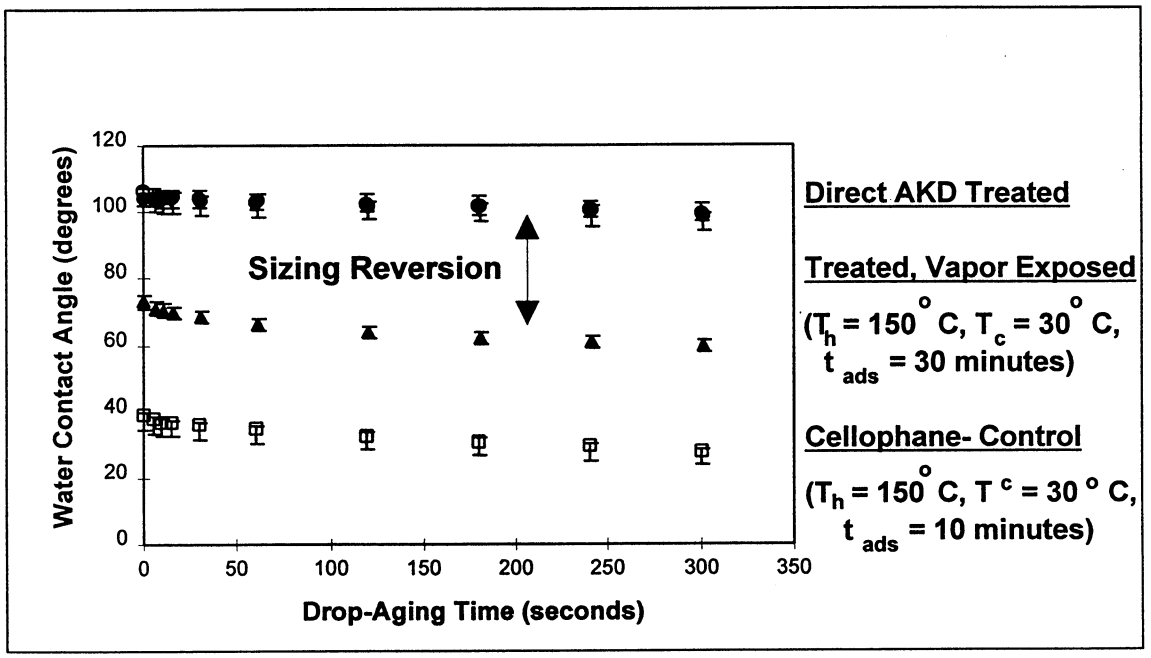

Figure 6. Water Contact Angle/Drop-Aging Time Comparison of AKD-Treated Cellophane with Cellophane Containing Volatile Products. Exposure to AKD volatile products gives a lower contact angle.

It is clear from Figure 6 that the water contact angle of the cured AKD-treated cellophane is much higher than that of the volatile product adsorbate and does not decrease as rapidly with time. None of the contact angles determined in this study approach the contact angle of cured AKD-treated cellophane. A lower contact angle than AKD suggests a loss in sizing efficiency, which, in turn, can be responsible for sizing reversion. It is apparent that the composition of the volatile product adsorbate is not pure AKD. The exact chemical composition of the adsorbates is the subject of the analytical portion of this research and will be reported separately.

Impact of Volatile Products on AKD Treated Cellophane

The direct bonding of AKD with cellulose is theorized to occur in the dryer section of the paper machine as most of the water is removed from the sheet and the AKD spreads on the fiber surface.[2, 13] Following surface spreading, the AKD is believed to orient itself with the hydrophobic tails outward from the fiber, thereby producing sizing. Under certain conditions, AKD may react with the cellulose hydroxyl groups and become anchored to the fiber surface. The surface energy of the surface is decreased as the high-energy fiber surface is masked by the lower energy AKD. Similarly, the process of sizing reversion can be the result of a higher surface energy volatile product adsorbing over the AKD layer and increasing the surface energy thereby giving a lower water contact angle. This concept was evaluated by comparing the contact angle of AKD-treated cellophane with that of the same film after exposure to AKD volatiles. The results are shown in Figure 7.

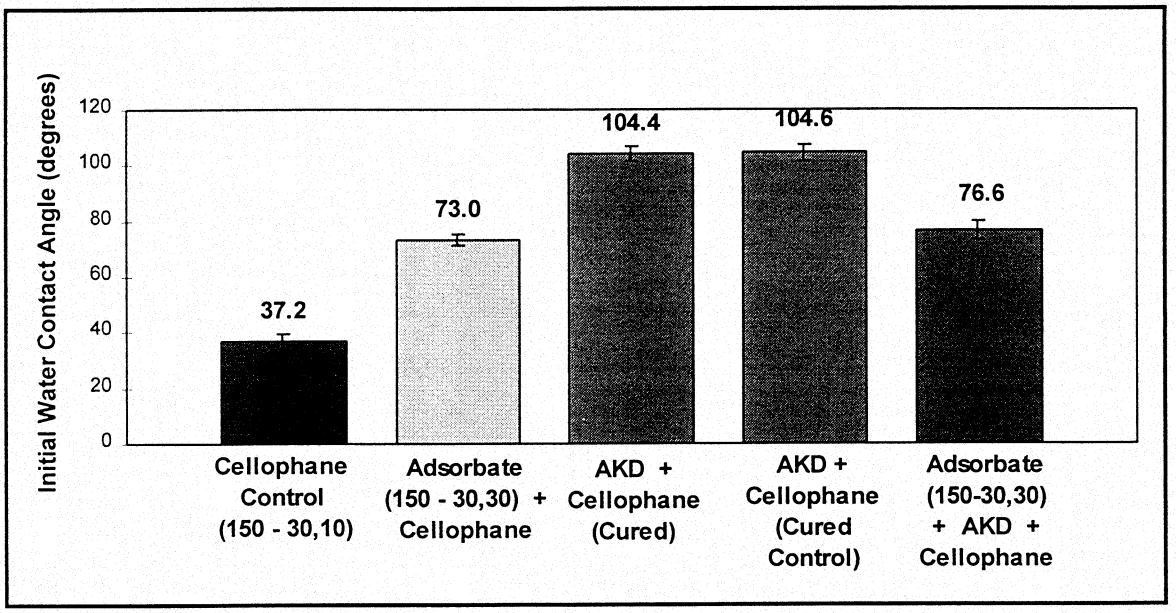

Figure 7. Reduction of Water Contact Angle of AKD-Treated Cellophane by the Adsorption of Volatile Products. Adsorption of volatile products from hot AKD onto cellophane previously treated with AKD decreases the water contact angle to the level observed for untreated cellophane.

In Figure 7, the initial water contact angle on cellophane is plotted for several experiments: (1) a control without AKD (T_h = 150°C, T_c = 30°C, t_{ads} = 10 minutes), (2) a typical result of film exposed to AKD volatiles (T_h = 150°C, T_c = 30°C, t_{ads} = 30 minutes), (3) a cured AKD-treated cellophane sample, (4) a cured AKD-treated cellophane control additionally heated under volatile product collection conditions without AKD (T_h = 150°C, T_c = 30°C, t_{ads} = 30 minutes), and (5) a cured AKD-treated cellophane exposed to AKD volatiles (T_h = 150°C, T_c = 30°C, t_{ads} = 30 minutes). Error bars are shown for 95% confidence intervals around the mean for two replicates.

The initial water contact angle of the cellophane control is relatively low at 37.2 +/- 2.7 degrees. Adding the volatile products from heating AKD, the initial water contact angle increases to 73.0 +/- 2.1 degrees. When AKD is deposited onto cellophane, the initial water contact angle rises to 104.4 +/- 2.7 degrees. Additional reaction of the AKD adsorbate at the vapor collection temperature (T_h = 150°C) has no effect on the initial water contact angle. When the volatile products from heated AKD collect on the cellophane containing AKD, the initial water contact angle falls to 76.6 +/- 3.5 degrees. The 95% confidence intervals around the means for the two experiments containing volatile products from heated AKD overlap such that the two initial contact angles are equivalent. These results suggest that for the conditions employed in these experiments, the surface energy is independent of the original surface when exposed to the volatile products of heating AKD. It does not matter whether the original surface is virgin cellulose or AKD-treated cellulose, the water contact angle will be similar after the adsorption of volatile products from heating AKD.

CONCLUSIONS

The results of this research show that heating AKD produces material that migrates through the vapor phase and causes sizing reversion. In general, adsorption of volatile products onto a cellulose film produces sizing levels well below that of AKD-treated cellophane. The AKD temperature was the only variable found to be statistically significant. Significant reduction in the water contact angle was not observed until the AKD temperature was increased to 150°C.

The initial water contact angle of a sample of a cellulose film previously treated with AKD decreased from 104.4 +/- 2.7 degrees to 76.6 +/- 3.5 degrees upon exposure to the volatile products from hot AKD. This level of sizing was similar to the water contact angle (73.0 +/- 2.1 degrees) of a virgin cellulose film sample exposed in a similar manner. The decrease in contact angle to similar levels indicates that the surface of a cellulose substrate can be modified independent of the state of the original surface and that the final contact angle is dependent on the composition of the adsorbed material.

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